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Title of invention

"Menetelmä keinotekoisen patinan valmistamiseksi ja patinapasta"

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METHOD FOR PREPARING AN ARTIFICIAL PATINA AND A PATINA PASTE

The present invention relates to a method for preparing an artificial patina paste to substrates, preferably made from copper or copper alloys and a patina paste made with the method.

Copper and copper alloys become covered with an oxide film in normal atmospheric conditions. Brown oxide and later green patina forms on copper outdoors with a varying rate depending on where and how the surface is exposed. Natural patina is the result of metal corrosion in the atmosphere. The patina film has a certain protective effect. It takes many years of exposure for green patina to form on a copper substrate. The time is especially long in a clean rural atmosphere, where the green patina may not form at all.

A large number of methods of artificial green patination have been described earlier. US patent 3,152,927 relates to a method and a paste in which a patina gel is formed of basic copper nitrate and ferric sulfate. Basic copper nitrate is not thermodynamically stable in rainwater but this changes gradually to stable basic copper sulfate. The colour of basic copper sulfate and nitrate is blue and iron is used to give green colour to the product. The patina paste is spread on an oxidized copper surface.

US patent 5,160,381 describes a method in which artificially formed patina on copper is formed by a) removing impurities, b) polishing with a mixture of acetic acid, copper sulfate, sodium chloride, sodium hydroxide, and copper acetate until a brown colour is obtained c) washing the polish copper substrate, d) brushing and e) after drying submitting said substrate to a filtered solution of hydrochloric acid, copper carbonate, ammonium chloride, copper acetate, arsenic trioxide and copper nitrate.

US patent 5,714,052 relates to a method for producing brochantite patina on copper by using the copper precursor material as copper coils as an anode in an electrolysis bath, containing for example sodium carbonate. During this step, a green carbonate-sulfite patina is produced on the precursor material. The material is rinsed and moved through a fixing bath, in which the initially formed carbonate-sulfite patina is converted almost entirely into basic copper sulfate, i.e. into brochantite. The fixing bath contains at least one of the oxidation agents: hydrogen peroxide, potassium chlorate, potassium peroxodisulfate, potassium permanganate and copper sulfate.

US patent 6,176,905 relates to a process and reaction solution for especially pre-oxidized or partially already patinated copper surfaces. The copper surfaces are applied with a reaction solution comprising an aqueous solution of a copper salt and a basic salt. The well-suited copper salts are copper(I)carbonate, copper(II)carbonate, copper(I)chloride, copper(II)-chloride, copper(II)sulfate, copper acetate, copper nitrate or mixtures thereof. The basic salt is selected from the group consisting of potassium carbonate, sodium hydrogen carbonate, potassium hydrogen carbonate, sodium sulfate etc.. The reaction solution of the example contains copper sulfate, sodium carbonate and sodium chloride.

WO application 95/29207 discloses a process for patina formation in which copper sulfate and optionally iron sulfate react with an inorganic hydroxide compound and after that a suitable binder is used. The binder is added to the patina before the patina is spread onto the substrate. The binder is inorganic silicate and its amount is from 100 to 1000 g patina powder per liter binder. A carboxylic acid can be used as a further assistant in adhesion.

US patent 5,691,001 relates to a method for surface treatment of a copper bearing material. A precipitate is formed by mixing an aqueous solution of at least one copper salt and alkali metal hydroxide, the precipitate is filtered and washed by a capillary filtering. The solids content of the precipitate is

adjusted within the range of 15 – 50 % by weight and the precipitate is stored at a temperature below 5°C until just the surface treatment of the copper bearing material.

As was said before, basic copper nitrate is not thermodynamically stable but it changes gradually to more stable basic copper sulfate caused by sulfates from the rainwater or from the oxidation reaction of sulfur dioxide on the metal surface. However, content of sulfur dioxide in the atmosphere has nowadays diminished due to improved air pollution control and so the change from basic copper nitrate to basic copper sulfate takes more time. In low pollution areas part of the patina can be lost by run off and also discoloration can occur during the transform period.

The first cited method uses iron salts for giving the green colour tinge for the patina because both basic copper nitrate and sulfate precipitates are blue in colour without iron. Problem with iron addition is the formation of rust and due to that discolouring of the patina surface. Iron compounds also make the patina layer more oxidizing, which is beneficial for the formation of new patina during exposure. Adequate oxidizing effect is achieved with less iron compared to the amount required for the green colour tinge.

The present invention relates to a method for producing an artificial patina paste and an artificial patina paste. According to the method, the patina is made of at least one copper salt and, which is precipitated with alkali metal hydroxide. The copper salt is optionally copper sulfate but it may also be copper nitrate, copper chloride, copper carbonate or a mixture of them. The reaction of copper salt and alkali metal hydroxide is stopped with water. The sludge is then washed and dried with a suitable filter for forming a precipitate. A capillary filter and the solids content from about 15 to 50 % are advisable.

Now we have also noticed that it is preferable to disperse the precipitate with effective mixing in a dispersion equipment possibly with the addition of dispersing agent. The dispersion agent can be a suitable commercial product. This separates the agglomerated particles of the precipitate and prevents re-agglomeration. The dispersion of the precipitate makes the ready paste easy to spread. Another advantage of the dispersion is that the paste is storable at room temperatures instead of earlier refrigerator temperatures. In addition, also the shelf life increases, from four weeks to several months, for example six months.

An addition of a suitable oxidative chemical agent to the sludge (precipitate) is preferential as well as to use agents like carbon, which catalyze forming of sulfate from sulfur dioxide in the atmosphere.

The essential features of the invention will be made apparent in the attached claims.

An iron salt can possibly also be used as a raw material of patina paste. The iron salt is optionally iron(III)sulfate but it may also be iron (III)nitrate or iron(III)chloride.

We have noticed that precipitates having different grain size, grain form and grain size distribution can be achieved by adjusting of the concentration of chemicals and the feeding rate of the alkali metal hydroxide during the precipitation process. Grain size, grain size distribution and grain form have an effect on the colour shade and durability of the patina layer. The grain size of 0,2 – 100 μm has been proved out to be advantageous.

A suitable oxidative chemical agent is added to the sludge (precipitate). This is done before or after the dispersion, depending on the agent used. In addition to the oxidizing function of these agents they also act as colouring agents. The oxidative chemical agent in this case can be iron compound but

as the main oxidative agent it is advantageous to use for example manganese dioxide (MnO_2). Iron can be added as iron hydroxide, iron(III)oxide or mixtures thereof. Also commercial mineral pigment compounds containing these oxidizing agents can be used. The object of this addition is to make the sludge more oxidizing, which is favorable to the stability and adherence of the patina layer. By adding other oxidative chemicals it is now possible to make a patina paste without iron or less than conventionally and to diminish rust formation and discolouring problems.

It is also preferable to use agents, which catalyze forming of sulfate from sulfur dioxide in the atmosphere i.e. which add prerequisites for natural patina forming. Such catalyst is for example carbon. Carbon can be added as coal powder, soot or graphite. Also commercial pigment like Mineral Black ($C+SiO_2$) or Black Earth (C) can be used. Carbon additions also have an effect on the colour of the paste.

In addition to the colour effect of the oxidizers and catalysers mentioned above, it is advantageous to use also other stable metal compounds for achieving the desired colour. As the basic sulfate and basic nitrate precipitates of copper are blue in colour, additions of yellow or brown particles make it greener. Yellow colour pigments based on stable metal compounds have more powerful colouring effet on the paste compared to the iron compounds in the precipitate process. It is advantageous to use for instance pigments like Mars Yellow ($Fe_2O_3 \cdot H_2O + Al_2O_3$), Yellow Ochre ($Fe(OH)_3$) , Raw Amber Earth ($Fe_2O \cdot MnO_2 \cdot nH_2O + Si + Al_2O_3$) or Siena Natural Earth ($Fe_2O_3 \cdot nH_2O + MnO_2 + Al_2O_3 + SiO_2 \cdot 2(H_2O)$) instead or in addition to the iron put in the precipitation process. Also brown pigments like Iron Brown (Fe_2O_3), Manganese Brown (MnO_2, Mn_2O_7), Sienna Burnt ($Fe_2O_3 \cdot nH_2O + Al_2O_3 + MnO_2$), Burnt Umber ($Fe_2O_3 \cdot MnO_2 \cdot nH_2O + Si + Al_2O_3$) can be used likewise. Magnetite and tenorite (CuO) give nice dark shade for the green paste. For example Malachite Green ($CuCO_3 \cdot Cu(OH)_2$), Opaq Chromium Green (Cr_2O_3), in which chromium is its trivalent form,

Chrysocolla ($CuSiO_3 \cdot nH_2O + Cu_2CO_3(OH)_2 + CuCO_3(OH)_2$) and Green Earth (Mg, Al, K) are pointed out to be stable inorganic mineral pigments for green colour. The amount of the metal compounds used as pigments is minor, usually below 1 % of the patina paste precipitate.

When copper sulfate is used as a raw material of patina paste, the reaction with alkali metal hydroxide form brochantite ($Cu_4SO_4(OH)_6$) or posnjakite ($Cu_4SO_4(OH)_6 \cdot 2H_2O$). Posnjakite is a product forming in nature and it changes gradually to brochantite during some years. It may be advantageous to have also posnjakite in the patina since it gives more vividness to the surface when changing to brochantite.

In preparation of patina, it is also a purpose that patina adherence to the substrate is good and that patina surface is durable. This can be improved by adding a binder to the patina paste. Sodium silicate has been commonly used as a patina binder and it has been sprayed onto the patina surface after the patina has been spread on the substrate. Now we have noticed that it is advantageous to use an alkyd-based compound as a binder and add it to the proper patina paste during the pasta preparation. Adding of the binder to the paste in connection of preparation does not shorten the storage time. The amount of the binder is at highest 10 % of the patina paste dry matter, preferably 2 – 3%. The amount of dry matter in the patina paste is from 15 – 50%. The amount of binder is so adjusted, that after application the patina layer is firmly attached to the substrate. The patina particles are not totally but only partially covered by the binder. This leaves the patina paste particles exposed to the atmosphere so that natural patination reactions can proceed.

Using of binder is not always necessary but advisable. The grain size of the patina paste has significance to the durability of the patina surface. Some test campaigns with posnjakite as the main component, grain size with flat distribution curve between 0,2 – 80 µm gave good results. This type of paste

gives very durable patina layer with good adherence even without any binder.

Patina gel according to this invention can easily be applied with brush, roller or spraying. The paste also is storable for prolonged times in ambient temperatures. The paste can be used in on site application as well as for prepatinated elements or sheets. The durability of the patina layer achieved makes it possible to form the patinated sheets and make profiles for architectural usage. The oxidative agents and catalysing carbon compounds in the patina layer aid natural reactions with the atmosphere and the formation of new natural patina.

The invention is described more by aid of the following examples:

Example 1

The precipitation process is carried out in a reactor of five cubic metres. Proper mixing is achieved with an agitator placed about 400 mm above the bottom of the reactor. This makes it possible to use considerably low concentration in the process solutions if wanted. This is important if we want to make batches of different grain size and grain form.

475 liters of tap water is added to the reactor. 100 kilos of copper sulfate with 27 % of copper is mixed in with constant agitation. After the copper sulfate is completely dissolved, 4kg of ferric sulfate with 21-23% of iron is added. 714 liters of 1 mol sodium hydroxide solution is pumped in the reactor and the precipitation is allowed to happen. The process is stopped by pumping in 1960 liters of tap water. The precipitate is allowed to settle for a few hours. The clear liquid is pumped off and the precipitate is taken to a chemical filter for washing. After the washing and filtering, the precipitate contains 20 to 30 % of solids and less than 0.1 % of alkaline ions.

This precipitate is pumped into a dissolver for dispersion. 200 g of carbon powder, 300 g of manganese dioxide (MnO_2), 1litre of Malachite Green ($CuCO_3 \cdot Cu(OH)_2$) and 2 litres of commercial dispersing agent is added. After the dispersion process 15 litres of alkyd binder in water solution is added with slow mixing. The product is mainly brochantite with 20 to 30 % of solids with a grain size of 0,5 to 12 microns. The product is packed in plastic barrels and stored in room temperature.

This product was applied to three sets of brown oxidized copper plates. The application was made with brush, brush and roller and with spray gun respectively. Two plates of each set and were taken to a cabinet test. Brown oxidized plates and bare copper plates were put in as references.

Cabinet test :

Solution: artificial rainwater

chemical	mmol
NaCl	10.0000
NH_4NO_3	0.0400
K_2SO_4	0.0031
$MgSO_4 \cdot 7H_2O$	0.0049
$CaSO_4 x 2H_2O$	0.0050
H_2SO_4	0.0230

Temperature: 50°C

Spray: 30 min/h at a rate of 0.8l/h

Duration 250 h

Visual inspection after the test showed, that all the patinated samples were almost intact. The bare copper samples had turned dark brown. The oxidised plates had white areas and some loss of black oxide on the surfaces, like we have seen on oxidised copper samples exposed for two years at our marine corrosion station.

PATENT CLAIMS

1. A method for preparing an artificial patina paste to substrates preferably made of copper or copper alloys, in which method at least one copper salt is used as a raw material and precipitated with an alkali metal hydroxide, the formed sludge is filtered for forming a precipitate, **characterized** in that the reaction between the raw material and the alkali metal hydroxide is stopped with water, the precipitate is dispersed with powerful mixing and an addition of a dispersing agent, and in addition, both an oxidative agent is used and carbon as an agent for catalysing natural patina forming.

2. A method according to claim 1, **characterized** in that at least one of the group including copper sulfate, copper nitrate, copper chloride, copper carbonate ore their mixture is used as the raw material of the artificial patina paste.

3. A method according to claim 1 or 2, **characterized** in that copper sulfate is used as the raw material of the artificial patina paste.

4. A method according to any of the preceding claims, **characterized** in that manganese dioxide is used as an oxidative agent.

5. A method according to any of the preceding claims, **characterized** in that an iron compound is used as a raw material of the artificial patina paste.

6. A method according to any of the preceding claims, **characterized** in that iron compound is used as an oxidative agent.

7. A method according to any of the preceding claims, **characterized** in that at least one stable metal compound is used as colour pigments.

8. A method according to claim 7, **characterized** in that iron compound pigments are used as yellow colour pigments.

9. A method according to claim 7, **characterized** in that iron and aluminium compound pigments are used as yellow colour pigments.

10. A method according to claim 7, **characterized** in that iron and manganese and aluminium compound pigments are used as yellow colour pigments.

11. A method according to claim 7, **characterized** in that iron and/or manganese compound pigments are used as brown colour pigments.

12. A method according to claim 7, **characterized** in that iron and manganese and aluminium compound pigments are used as brown colour pigments.

13. A method according to claim 7, **characterized** in that copper compound pigments are used as green colour pigments.

14. A method according to claim 7, **characterized** in that chromium(III) compound pigments are used as green colour pigments.

15. A method according to any of the preceding claims, **characterized** in that an alkyl-based compound is used as a binder and the binder is added to the patina paste during the paste preparation.

16. A method according to claim 15, **characterized** in that the amount of the binder is at highest 10% of the patina paste dry matter.

17. A method according to any of the preceding claims, **characterized** in that the amount of dry matter in the patina paste is between 15 – 50%.

18. An artificial patina paste to substrates preferably made of copper or copper alloys wherein at least one copper salt is used as a raw material, **characterized** in that the paste contains an oxidative agent, and carbon for catalysing natural patina forming and that an alkyl-based compound is used as a binder.

19. A patina paste according to claim 18, **characterized** in that at least one of the group including copper sulfate, copper nitrate, copper chloride, copper carbonate ore their mixture is the raw material of the patina paste.

20. A patina paste according to claim 18 or 19, **characterized** in that copper sulfate is the raw material of the patina paste.

21. A patina paste according to claim 18 or 19, **characterized** in that a part of the patina paste is posnjakite ($Cu_4SO_4(OH)_6 \cdot 2H_2O$) with a grain size between 0,2 – 80 µm.

22. A patina paste according to claim 18, **characterized** in that a grain size of the patina paste particles is between 0,2 – 100 µm.

23. A patina paste according to claim 18, **characterized** in that the amount of dry matter in the patina paste is between 15 – 50%.

24. A patina paste according to claim 18, **characterized** in that the binder covers only partially the patina paste particles.

25. A patina paste according to claim 18, **characterized** in that at least one stable metal compound is used as colour pigments.

26. A patina paste according to claim 25, **characterized** in that iron compound pigments are used as yellow colour pigments.

27. A patina paste according to claim 25, **characterized** in that iron and aluminium compound pigments are used as yellow colour pigments.

28. A patina paste according to claim 25, **characterized** in that iron and manganese and aluminium compound pigments are used as yellow colour pigments.

29. A patina paste according to claim 25, **characterized** in that iron and/or manganese compound pigments are used as brown colour pigments.

30. A patina paste according to claim 25, **characterized** in that iron and manganese and aluminium compound pigments are used as brown colour pigments.

31. A patina paste according to claim 25, **characterized** in that copper compound pigments are used as green colour pigments.

32. A patina paste according to claim 25, **characterized** in that chromium(III) compound pigments are used as green colour pigments.

33. A patina paste to claim 18, **characterized** in that the amount of the binder is at highest 10% of the patina paste dry matter.

34. A patina paste according to claim 18, **characterized** in that the storage time is several months.

35. A patina paste according to claim 18, **characterized** in that the paste is storable in room temperature.

ABSTRACT

The present invention relates to a method for preparing an artificial patina paste to substrates, preferably made from copper or copper alloys and a patina paste. The raw material is a copper salt, which react with an alkali metal hydroxide. The precipitate is dispersed with powerful mixing and an addition of a dispersing agent. An oxidative agent like manganese dioxide is used, and carbon is used as an agent for catalysing natural patina forming. The invention relates also the patina pasta, in which alkyl-based compound is used as a binder.